Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202113498

Link to VoR: https://doi.org/10.1002/anie.202113498
Nanoconfinement Engineering over Hollow Multi-Shell Structured Copper towards Efficient Electrocatalytical C-C coupling

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Abstract

Nanoconfinement provides a promising solution to promote electrocatalytic C-C coupling, by dramatically altering the diffusion kinetics to ensure a high local concentration of C\textsubscript{1} intermediates for carbon dimerization. Herein, under the guidance of finite-element method simulations results, a series of Cu\textsubscript{2}O hollow multi-shell structures (HoMSs) with tunable shell numbers were synthesized \textit{via} Ostwald ripening. When applied in CO\textsubscript{2} electroreduction (CO\textsubscript{2}RR), the \textit{in-situ} formed Cu HoMSs showed a positive correlation between shell numbers and selectivity for C\textsubscript{2+} products, reaching a maximum C\textsubscript{2+} Faradaic efficiency of 77.0 ± 0.3% at a conversion rate of 513.7 ± 0.7 mA cm\textsuperscript{-2} in neutral electrolyte. Mechanism studies clarified the confinement effect of HoMSs that superposition of Cu shells leads to a higher coverage of localized CO adsorbate inside the cavity for enhanced dimerization. This work provides valuable insights for delicate design of efficient C-C coupling catalysts.

Keywords: nanoconfinement; diffusion kinetics; CO\textsubscript{2} electroreduction; C-C coupling
The anthropogenic fossil fuel consumption and excessive emission of CO$_2$ have aroused the concerns of energy crisis and environmental damage. Direct conversion of CO$_2$ into value-added chemicals and fuels, powered by renewable electricity, offers possibility to simultaneously reduce overdependence on fossil fuels and close the anthropogenic carbon cycle.[1-4] Over the past years, major advances have been made in electrocatalytic CO$_2$ reduction (CO$_2$RR) to carbon monoxide (CO)$^{[5-8]}$ and formic acid (HCOOH)$^{[9-12]}$ with high yield and near unity selectivity. Compared to C$_1$ products, deeply reduced C$_2^+$ products possess higher energy density and market value, thus sparking significant research interest. Copper (Cu) is recognized as the unique metal to efficaciously break the stable CO$_2$ bonds and to form C-C bonds, a key step towards C$_2^+$ products.$^{[13-17]}$ However, due to the sluggish kinetics of multiproton coupled electron transfer and C-C coupling steps, selective conversion of CO$_2$ into higher-value C$_2^+$ hydrocarbons and oxygenates at commercially relevant current density (>500 mA cm$^{-2}$) is still knotty.

The C-C coupling step is greatly affected by the adsorbed CO intermediates (*CO).$^{[18]}$ In general, when CO$_2$ molecule is converted to COOH*, the as-derived CO* will dictate the pathway to branch either to C$_1$ (e.g., CH$_4$) or C$_2$ (e.g., C$_2$H$_4$, C$_2$H$_5$OH) products. Hydrogenation of *CO to *CHO leads to C$_1$ products, whereas *CO dimerization to form *OCCO embarks on the C$_2$ pathway.$^{[18]}$ Given that the surface coverage of *CO correlates closely with the dimerization process, one would intend to increase the local concentration of CO to ensure a sufficient coverage of *CO for dimerization. For example, tandem catalysts have been adopted, in which one site produces high concentration of CO and subsequently being dimerized to C$_2$ species on another site.$^{[19, 20]}$ Alternative approach is to create a nanoconfinement space in Cu, whereby the intimate contacts and interactions between CO adsorbates increase the incidence of dimerization compared to open surface.$^{[21, 22]}$ Of note, the construction of nanoconfinement depends strongly on morphological control and nanoscale adjustment. Nevertheless, the reported Cu cavities mostly comprise of a single layer with large opening holes, leaving a lot of room and chance for the escape of CO adsorbates.$^{[21, 22]}$ Moreover, the presence of Cu$^+$ within the cavity, which is proposed to stabilize CO* and promote dimerization, might complicate the net contribution from nanoconfinement.$^{[22]}$

Here, we introduce a Cu hollow multi-shell structures (HoMSs), with shell number facilely tunable from 1 to 3, which serves as a simple and flexible platform to decipher the nanoconfinement effects on CO$_2$RR. Cu HoMSs is an integration of nanoshells layer by layer, with
nanovoids confined in between. As the shell number increases, the outflux of carbon species encounters with higher diffusion resistance and undergoes longer diffusion path length, rendering the localized C1 intermediates more vulnerable to dimerization.\textsuperscript{[23]} Enlightened by that, we firstly exerted finite-element method simulations to study the nanoconfinement effect on the distribution of key species of CO\textsubscript{2}RR over HoMSs. Experimentally, Cu\textsubscript{2}O HoMSs with tunable shell numbers were prepared \textit{via} Ostwald ripening, which was then subjected to \textit{in-situ} reduction under CO\textsubscript{2}RR. The as-formed Cu HoMSs showed improved selectivity towards C\textsubscript{2+} products as shell number increases, achieving a maximum C\textsubscript{2+} FE of 77.0 ± 0.3% at a partial current density of 513.7 ± 0.7 mA cm\textsuperscript{-2} in neutral electrolyte. Mechanism studies unraveled that superposition of Cu shells led to an increased surface coverage of CO adsorbates for more efficient carbon dimerization, agreeing well with the simulation results.

![Figure 1](image)

\textbf{Figure 1.} a) The FEM simulated species C\textsubscript{2}/C\textsubscript{1} concentration ratio distribution over single 1-shell, b) 2-shell, and c) 3-shell Cu HoMSs, respectively. The white dash lines represent Cu shells. Scale bar, 100 nm. d) Ratio of C\textsubscript{2}/C\textsubscript{1} productivity, measured by the total outflux of C\textsubscript{1} and C\textsubscript{2} products, as a function of shell number. e) Schematic shows how the confinement effect over multi-shell nanostructures promotes C\textsubscript{1} species binding and further conversion to C\textsubscript{2}.

We anticipate that by increasing the shell numbers of HoMSs, the diffusion kinetics might be dramatically retarded and the retention time of C\textsubscript{1} intermediates prolonged, bolstering the odds for further dimerization into C\textsubscript{2} products. To testify the hypothesis, we firstly implemented finite-element method (FEM) simulations to track the key species of CO\textsubscript{2}RR over HoMSs. Three models of HoMSs with 1-3 shells were established respectively, to simulate the mass transport of C\textsubscript{1} and
C₂ species around individual particle. In the simulations, we posit that CO₂ molecules diffuse into the multi-shell nanostructures, undergo adsorption and then evolve into C₁ species. The C₁ species might either desorb from the surface as a C₁ product, or dimerize to form a C₂⁺ product.

With the increase of shell number, we found that more C₁ intermediates are concentrated inside the cavity, substantially enhancing the probability of C-C coupling towards C₂ products (Figure S1). Figures 1a-c shows the corresponding C₂/C₁ ratios distributed across the three HoMSs respectively, which exhibits a positive dependence on the shell numbers (Figure 1d). Specifically, the C₂/C₁ ratio of 3-shell is 5.6 and 1.9 times higher than that of 1-shell and 2-shell, respectively. Moreover, when the simulation parameters such as kinetic constants, equilibrium constants and diffusion coefficients are altered, the trend of C₂/C₁ ratio as a function of shell number still holds (Figure S2). Since the same electric potential was applied over the HoMSs with 1-3 shells (Figure S3), suggesting that the catalytic activities were kept constant, the diffusion process as a function of nanoconfinement might account for the disparity of products distribution. Accordingly, we inferred that although HoMSs with 1 shell might locally confine certain amounts of C₁ adsorbates inside the cavity to form C-C bond, nevertheless, there is still a big chance for the outflux of desorbed C₁ species as final C₁ products. As such, increasing the shell number could increase the diffusion hurdles and extend the diffusion path length, which effectively restricts the outflux of locally produced C₁ species (Figure S4). As a result, the entrapped C₁ intermediates with a high local concentration could dimerize to C₂⁺ products against great odds (Figure 1e). Altogether, the simulation results validate the function of nanoconfinement as a feature of HoMSs on promoting carbon dimerization towards C₂⁺ products.
Figure 2. a) Schematic diagram illustrates the design of constructing Cu$_2$O HoMSs. b) TEM images of 1-shell Cu$_2$O, c) 2-shell Cu$_2$O, and d) 3-shell Cu$_2$O, respectively. Scale bars, 100 nm. e) The X-ray photoelectron spectra of Cu LMM of the as-prepared Cu$_2$O HoMSs.

Under the guidance of simulation results, Cu$_2$O multi-shell nanostructures with different numbers of layers were synthesized. In details, CuSO$_4$ was used as the Cu precursor and dissolved in water at room temperature, which can be reduced to form Cu$_2$O nanoparticles by adding N$_2$H$_4$·H$_2$O as the reducing agent. Cu$_2$O single-layer nanoshells were then obtained from the first-step Ostwald ripening process. As illustrated in Figure 2a, after the introduction of N$_2$H$_4$ into the reacting solution, newly formed Cu$_2$O nanocrystallites were assembled inside and outside the first nanoshell layer to form a thicker nanoshell. When a second Ostwald ripening process occurred, both the inner and the outer shells would become thinner gradually, leading to the formation of
double-shell nanostructures.[24] Nanospheres with rough and porous surface were observed by using scanning electron microscopy (Figure S5). Transmission electron microscope (TEM) images in Figures 2b-d revealed multi-shell nanostructures with single, double and triple layers respectively. To confirm the chemical state of Cu in the HoMSs, a series of X-ray measurements were conducted on the derived samples. The X-ray diffraction patterns confirmed cubic Cu$_2$O phase in all the multi-layer nanoshells (Figure S7). The spectra of Cu 2p (Figure S8) and Auger Cu LMM (Figure 2e) conducted by X-ray photoelectron spectroscopy, taken together, identified the state of Cu$^+$ in Cu$_2$O HoMSs.

![Figure 3](image)

Figure 3. a) CO$_2$RR products distribution on the catalysts possessing 1-3 shell HoMSs (denoted as 1-3 here, respectively) at different applied potentials. (b) C$_2$ partial current densities obtained on HoMSs at different applied potentials. (c) C$_2$/C$_1$ product selectivity on HoMSs, showing that 3-shell HoMSs has the largest C$_2$ selectivity. (d) Durability test of 3-shell HoMSs for 8 h of CO$_2$-electrolysis in 0.5 M KHCO$_3$ at a current density of -300 mA cm$^{-2}$.

Catalytic activity and selectivity of HoMSs towards electrocatalytic CO$_2$ reduction were investigated in a flow reactor using 0.5 M KHCO$_3$ solution as electrolyte. Before the test, the as-prepared Cu$_2$O HoMSs loaded on the carbon gas diffusion layers (GDL) was firstly subjected to an electroreduction under -0.82 V vs. RHE for 10 mins, with their morphologies still conserved (Figure S9). Linear scanning voltammetry (LSV) of the as-reduced HoMSs under Ar and CO$_2$
atmosphere, respectively, were conducted firstly to examine CO$_2$RR activity by comparing the polarized current, which indicates the kinetics of cathodic reduction. According to the polarization curves measured by LSV, a remarkable enhancement of polarized current in CO$_2$ environment was observed (Figure S10). In addition, the reduction current of HoMSs with different layers manifested almost the same intensity, meaning a similar activity to catalyze CO$_2$RR.

Then the electrolysis gas and liquid products under different potentials were detected by an online gas chromatography and the nuclear magnetic resonance $^1$H spectrum, respectively. As a result, we obtained an CO$_2$RR products distribution of HoMSs, involving C$_2$+ (C$_2$H$_4$, C$_2$H$_5$OH, CH$_3$COOH and C$_3$H$_8$O), C$_1$ (CO and formate) and H$_2$ (Figure S11). Further analysis delivered the FE and partial current density of C$_1$ and C$_2$+ species over HoMSs towards CO$_2$RR (Figures 3a-b). The 1-shell HoMSs catalyst exhibited a maximum C$_2$+ FE of 40.3 ± 1.0% at -0.88 V vs. RHE with a C$_2$+ current density of 268.8 ± 6.7 mA cm$^{-2}$. In contrast, the 2-shell HoMSs reached a maximum C$_2$+ FE of 62.2 ± 0.3% with a C$_2$+ current density of 414.8 ± 2.2 mA cm$^{-2}$, while the 3-shell HoMSs sample showed a maximum C$_2$+ FE of 77.0 ± 0.3% with an impressing C$_2$+ current density of 513.7 ± 0.7 mA cm$^{-2}$ under the same potential.

As the measured C$_2$+/C$_1$ ratio summarized in Figure 3c, the increasing shell number promoted the C$_2$+ production obviously. In order to exclude the influence of active sites amount, we compared the intrinsic activities of Cu sites in HoMSs with electrochemical active surface areas (ECSA) normalization which was determined by the underpotential deposition of Pb (Figure S12). The ECSA-normalized C$_2$+ partial current density of three catalysts were also calculated, which substantiated the superior intrinsic activity on 3-shell HoMSs in accordance with our previous conjecture (Figure S13). Moreover, the 3-shell HoMSs catalyst also possessed a conspicuous durability. An 8-hour stability test over 3-shell HoMSs was executed at a constant current density of -300 mA cm$^{-2}$, where the C$_2$+ FE and voltage potentials both remained steady (Figure 3d). The 8-h durability could be attributed to the buffering effect of HoMSs, which enhanced structural tolerance towards disturbance outwards.$^{[23]}$ More remarkably, the morphology of 3-shell HoMSs remained almost intact after long term electrolysis (Figure S14). Considering the unfavorable flooding of carbon GDL, the duration time could be expected to be further extended via loading the catalyst on PTFE membrane.
Figure 4. a) In situ Cu K-edge X-ray absorption near edge spectra of HoMSs under applied potentials. Ex situ Cu K-edge X-ray absorption spectroscopy of Cu$_2$O and metallic Cu were performed as standards. Among spectra of HoMSs, dash lines were collected at open circuit potential while solid lines were collected at -0.82 V vs. RHE. b) In situ Raman spectra of the 3-shell HoMSs catalyst during CO$_2$RR under different applied potentials. c) Comparison of in situ Raman spectra of 1-3 shell HoMSs at -0.82 V versus RHE in the range of 1900-2200 cm$^{-1}$.

In an effort to elucidate the real electronic structure of HoMSs under CO$_2$RR reaction conditions, we conducted in situ X-ray absorption spectroscopy (XAS) measurements. Figure 4a shows the Cu K-edge normalized absorption spectra of the HoMSs, which was in-situ reduced from Cu$_2$O HoMSs in a home-made XAS flow cell under -0.82 V vs. RHE (solid lines), or under open circuit potential (dash lines) as comparison. Copper foil and commercial Cu$_2$O were adopted as standard samples for Cu$^0$ and Cu$^1$ reference, respectively. Judging from the shift of adsorption edge and the shape of white line peaks, we inferred that the Cu$_2$O HoMSs with 1-3 shells were all reduced to metallic Cu from Cu$_2$O. Furthermore, the extended X-ray absorption fine structure of the HoMSs catalysts indicates that after the negative potential was applied, the peak ascribed to Cu-O bonds disappeared, while the peak representing Cu-Cu bonds arose (Figure S15). The above results brought forth the conclusion that the active phase of HoMSs under CO$_2$RR condition is metallic Cu, namely the Cu HoMSs catalyst.

To shed light on the possible mechanism underlying the confinement effect on CO$_2$RR, we
sought to perform detailed mechanism studies. At first, a current-step experiment was conducted, where the current was instantly stepped from reductive current to oxidative one. The appeared oxidative peak correlates with the oxidation of the localized intermediates.\textsuperscript{[25]} When the intermediates are more locally concentrated, the intensity of the oxidative peak increases accordingly. As the shell number of Cu HoMSs increases, the current step curves under CO\textsubscript{2} atmosphere shows a more intensified oxidative peak (Figure S16). Whereas in the case of 3-shell Cu HoMSs, the oxidative peak was absent under Ar atmosphere. This phenomenon led us to speculate that the Cu HoMSs with more shells holds superior capability to confine the carbon species.

Then we conducted \textit{in situ} electrochemical Raman spectroscopy to monitor the surface adsorbates during CO\textsubscript{2}RR process over Cu HoMSs. Figure 4b displayed \textit{in situ} Raman spectra of 3 shell-Cu HoMSs under varied potentials. On scanning the applied potential from -0.1 to -0.82 V vs. RHE over the 3-shell Cu HoMSs catalyst, a notable peak between 2060 cm\textsuperscript{-1} and 2070 cm\textsuperscript{-1} appeared, which was ascribed to the C≡O stretch of the linearly surface-absorbed CO, the key intermediates of C-C coupling.\textsuperscript{[22]} The peak intensities increased on scanning to more negative potentials, in line with the trend of C\textsubscript{2+} products formation rates (Figure 3b). Moreover, the \textit{in situ} Raman spectra of the Cu HoMSs with 1-3 shells were compared under the same potential (Figure 4c), where the peak intensity of surface-absorbed CO shows a monotonic increase with the shell number. The observations are consistent with the simulation and CO\textsubscript{2}RR results, that superposition of Cu shells led to the increased surface coverage of CO adsorbates for promoting C-C coupling.

The above results, taken together, conclude that the nanoconfinement effect is crucial for the carbon dimerization in CO\textsubscript{2}RR. When the reactant species in bulk space influx to the innermost cavity of HoMSs with multi-shells, the confinement space renders the intimate contact and interaction of reactants. Meanwhile, the outflux of as-formed carbon species, restricted by the retarded diffusion kinetics, would suppress desorption of C\textsubscript{1} intermediates, leading to localized C\textsubscript{1} intermediates of high concentration for efficient dimerization towards C\textsubscript{2+} products. Moreover, considering that the synthesis of HoMSs is flexibly tunable, we anticipate by delicately engineering a cascade catalyst on HoMSs, the C-C coupling could be further dramatically enhanced.\textsuperscript{[23]}

In conclusion, we disclosed a correlation between the CO\textsubscript{2}-to-C\textsubscript{2+} conversion and nanoconfinement effect of Cu HoMSs with shell number tunable from 1-3. As the shell number
increases, the Cu HoMSs displayed a remarkable enhancement in both selectivity and activities towards C$_2^+$ species. Particularly, Cu HoMSs with 3 shells exhibits a maximum C$_2^+$ FE of 77.0 ± 0.3% with an impressing C$_2^+$ current density of 513.7 ± 0.7 mA cm$^{-2}$ in neutral electrolyte. Finite-element method simulation combined with experimental mechanism studies revealed that the increase of shell number leads to more CO adsorbate trapped inside nanovoids via retarding the diffusion kinetics. The resultant high local concentrations of C$_1$ intermediates were proposed to facilitate the C-C coupling process. Our work highlights the importance of nanoconfinement in carbon dimerization and provides guidance for designing highly efficient catalysts towards multicarbon products.

**Acknowledgements**

J.Z. acknowledges National Key Research and Development Program of China (2019YFA0405600), National Science Fund for Distinguished Young Scholars (21925204), NSFC (U19A2015), Fundamental Research Funds for the Central Universities, Provincial Key Research and Development Program of Anhui (202004a05020074), and USTC Research Funds of the Double First-Class Initiative (YD2340002002). C.X. acknowledges the University of Electronic Science and Technology of China (UESTC) for Startup funding (A1098531023601264), and the NSFC (22102018 and 52171201). T.Z. acknowledges NSFC (22005291).

**Conflict of interest**

The authors declare no conflict of interest.
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